

published in J. Electron Spectroscopy and Related Phenomena 183,48–52(2011)

Carbon K-shell Photo Ionization of CO: Molecular frame angular Distributions of normal and conjugate shakeup Satellites

T. Jahnke¹, J. Titze¹, L. Foucar¹, R. Wallauer¹, T. Osipov², E. P. Benis³, O. Jagutzki¹, W. Arnold¹, A. Czasch¹,
A. Staudte⁴, M. Schöffler², A. Alnaser², T. Weber², M. H. Prior², H. Schmidt-Böcking¹, and R. Dörner^{1*}

¹ *Institut für Kernphysik, University of Frankfurt,*

Max-von-Laue-Str. 1, D-60438 Frankfurt, Germany

² *Lawrence Berkeley National Laboratory, Berkeley CA 94720*

³ *Department of Physics, University of Ioannina, GR-45110 Ioannina, Greece*

⁴ *Stacie Institute for Molecular Sciences, NRC, 100 Sussex Drive, Ottawa, Ontario, Canada*

(Dated: January 18, 2013)

We have measured the molecular frame angular distributions of photoelectrons emitted from the Carbon K shell of fixed-in-space CO molecules for the case of simultaneous excitation of the remaining molecular ion. Normal and conjugate shake up states are observed. Photo electrons belonging to normal Σ -satellite lines show an angular distribution resembling that observed for the main photoline at the same electron energy. Surprisingly a similar shape is found for conjugate shake up states with Π -symmetry. In our data we identify shake rather than electron scattering (PEVE) as the mechanism producing the conjugate lines. The angular distributions clearly show the presence of a Σ shape resonance for all of the satellite lines.

I. INTRODUCTION

The present paper combines two vibrantly discussed topics: molecular frame angular distributions of inner-shell photoelectrons and few body processes induced by a single photon. We will ask how molecular frame angular distributions are influenced by the involvement of other active electrons and in turn what we can learn about few electron processes from molecular frame angular distributions. Before we discuss our experiment we give a brief summary on the background of both topics.

A. Photon induced many electron transitions

Photoionization of atoms and molecules leads in many cases to a simultaneous excitation of the remaining ion [1, 2]. Such ionization excitations manifest themselves in satellites lines to the main photoelectron line in the electron energy distribution. As this process is inherently a many electron process its description becomes particularly challenging: a widely used two-step model for ionization excitation implies that either the photon leads to the emission of the photoelectron by a primary *dipole* transition followed by a *monopole* transition inside the molecular ion (normal shake up). Alternatively the photon may excite the molecule in a *dipole* transition and subsequently an electron is shaken off to the continuum in a *monopole* transition (conju-

gate shake up). At high excess energies conjugate shake up dies off and only molecular ion states with the same symmetry as the ground state are populated. Conjugate shake up however contributes significantly at low electron energies.

The word "shake up" was introduced in the context of the sudden approximation. It refers to a "*mechanism*" by which the excitation proceeds. It can be formalized as a Feynman-diagram in many body perturbation theory [3–5]. In an intuitive picture of that description the photon induces a sudden single active electron transition in which it gives its angular momentum either to the ejected or the excited electron. This ionization or excitation step changes the potential and hence the eigenstates of the system. As the wave functions of the remaining electrons relax to the new eigenstates of the altered potential, they have a non zero overlap to excited or even continuum states to which they are "shaken up" or "shaken off". This simple picture, however, does not answer the question how the photon energy is partially transferred from the first electron, which absorbed the photon, to the shake electron, but it permits calculation of the shake probabilities as simple overlap integrals without an operator [2].

Within the framework of many body perturbation theory a second mechanism of electron-electron scattering, which actually has a classical analog, can lead to a two electron transition upon absorption of a single photon. This mechanism comes at a variety of names like TS1 [4], knock-off [6, 7] or PEVE (photoelectron valence electron interaction) [8–10]. It is also related to the rescattering mechanism in the multiphoton context [11]. The wording mechanism is certainly a simplification as the depicted scenario describes contributions

*Electronic address: doerner@atom.uni-frankfurt.de

to a transition amplitude. The details of these amplitudes have been worked out in great detail for the two electron process of single photon double ionization of helium [12].

Similar to the shake up mechanism, PEVE can be "normal" or "conjugate" which means that it can either lead to the same symmetry or to a different symmetry of the molecular ion compared to that of the main line. Such a change of symmetry is possible since the electrons can exchange angular momentum in the internal collision. For the case of a conjugate process PEVE and shake can be experimentally separated by examining the orientation of the molecular axis to the polarization [8]: if e.g. in the conjugate shake up the photon induces an excitation from a Σ to a Π orbital the molecular axis has to be perpendicular to the polarization during the photo absorption.

B. Molecular frame angular distributions

Angular distributions of photoelectrons emitted from molecules exhibit a very rich structure in the laboratory frame - if the molecular axis is fixed in space [13, 14]. What is the physical origin of this structure? From the perspective of angular momentum one may say that the outgoing photoelectron wave is a coherent superposition of several angular momentum states, even within the dipole approximation where only $1\hbar$ is deposited by the photon into the system. These high angular momenta in the continuum electron wave function are compensated by a rotational excitation of the molecular ion left behind, which can also be measured directly [15]. One may say that the photoionization process splits the many body wave function of electrons and nuclei of the neutral molecule into an angular momentum entangled wave function of a free electron carrying angular momentum in the angular distribution and a molecular ion carrying the equivalent angular momentum in rotation. A simplistic and mechanistical way to understand the creation of these high angular momentum states is suggested by the multiple scattering picture: a dipolar photoelectron wave is created in the K-shell of the molecule. On the way through the molecule this wave is multiply scattered at the multi center potential of the molecule. It is this multiple scattering which creates the angular momentum in the rotational degrees of freedom of the molecular ion and in the electron wave itself. In a particle picture the minima and maxima in the electron angular distribution are then interpreted as destructive or constructive interference between different pathways of the electron through the molecular environment. In a wave formulation they are the interference pattern of the direct dipolar electron wave with all multiply scattered electron waves. Such multiple scattering effects can be employed to use the photoelectron angular distribution to illuminate a molecule from within [16]. Particularly rich patterns

arise when the electron wave resonates inside the structure of the multicentric potential giving rise to a *shape resonance* [14, 17]. For homonuclear molecules, there is a second mechanism which gives rise to higher order angular momenta: the coherent emission of the primary electron wave from two or more centers. Even if multiple scattering is small, as it is e.g. the case for protons as scatterers in H_2 , this potentially delocalized nature of the photoeffect [18] alone can create diffraction structures in the angular distributions [13, 19–22] and hence also rotationally excite the ions.

C. Carbon K-shell ionization of CO

In the remainder of this paper we have chosen the example of Carbon K-shell ionization of fixed in space CO to investigate the interplay between creation of satellite lines via excitation with the molecular frame angular distributions. It is certainly tempting to try to understand the angular distribution of the satellites as being created by two steps: first an initial *p*-wave or *s*-wave of an outgoing electron is created by shake or conjugate shake process respectively and in a second step this low angular momentum wave is multiply scattered in the molecular potential where higher angular momenta are added. This simplistic picture, however, neglects the molecular symmetry of the wave functions. Our data show that an alternative view, also put forward in [23] is more appropriate. The *s*-wave character for the shaken off electron in the atomic case refers to the fact that no angular momentum is transferred from the photon to the shaken off electron. For the molecular case, where *s* is not a good quantum number, that idea can be generalized to shake up in which the Σ and Π character of the bound state wave function is conserved upon the transition to the continuum.

The Carbon K satellite spectrum of CO has been studied in detail experimentally [23–29] and theoretically [29–33]. Two major satellite features S0 and S1 corresponding to singlet and triplet coupled excitations have been observed [27] and calculated [32]. They show a very different photon energy dependence. High resolution studies have then resolved the various states contributing to these two main features (see Fig. 1 below and Table 1). Hemmers *et al.* [24] have measured the β -parameters of the electron for these lines. They found that - as expected by the simple picture above - the satellite lines fall into two groups: those with $\beta = 0$ which are conjugate shake up satellites and those whose β is similar to the one of the main line which are direct (i.e. normal shake up) satellites. In our study presented here we measure the molecular ion angular distribution in addition. As outlined above this will clearly allow us to also pin down not only the symmetry (normal or conjugate) but also the excitation mechanism (shake versus PEVE). As a further step we will then investigate the electron angular distributions in the body

fixed frame. This will in particular allow identification of possible shape resonances.

II. EXPERIMENT

The experiment has been performed at beamline BL4 of the Advanced Light Source at Lawrence Berkeley National Laboratory using the COLTRIMS technique [34–36]. The photon energies employed where in a region of 290 eV to 320 eV, in all cases the light was linearly polarized. We have set the monochromator to a resolution of about 100 meV, sufficient to resolve the major features of the satellite spectrum. The photon beam is crossed at right angle with a supersonic CO beam. The photoelectron and both ions are guided by weak electric (12.3 V/cm) and magnetic (8 G) fields towards two large area position and time sensitive micro channel plate detectors equipped with delayline position readout [37, 38].

In most cases the K shell ionization is followed by the emission of an Auger electron. The doubly charged molecular ion dissociates. For the further analysis we have selected only events where both ions were detected and the kinetic energy release was above 10.2 eV. In this case the dissociation proceeds along steeply repulsive curves and is rapid enough so that the molecular ion does not rotate between the photoelectron ejection and the fragmentation [39, 40]: the axial recoil approximation is valid. In that case the orientation of the molecule in the laboratory frame can be obtained. The two singly charged ions are emitted back-to-back in a Coulomb explosion. Therefore, by measuring the momenta of these two fragments the direction of the molecular axis at the instant of photo ionization is determined. During the offline analysis the measured electron momenta can be transformed from the laboratory frame to the molecular frame. Furthermore, a subset of the data where the molecular axis was oriented, for example perpendicularly, can be selected and plotted. That way molecular frame electron angular distributions from fixed in space molecules are obtained from an initially unoriented ensemble of molecules.

III. RESULTS

In Figure 1(a) we show the measured electron energy distribution at a photon energy of 318.97 eV in the region where satellite lines occur. The line positions with the assignment are taken from [24] and are given in Table 1. In [24] the β parameters of the electrons for the respective satellite states are measured. On this basis conjugate shake up states are identified by their isotropic angular distribution of the electron in the laboratory frame. Hemmers *et al.* took this as an indication that the electron results from a monopole transition. We list the known configurations for the

Peak	Assignment	Binding energy (eV)	type
0	$2\sigma^{-1} {}^2\Sigma^+$	296.20	Main
1	$2\sigma^{-1}5\sigma^{-1}2\pi^1(S' = 1)^2\Pi$	304.10	conjugate
2	$2\sigma^{-1}1\pi^{-1}2\pi^1(S' = 1)^2\Sigma^+$	304.85	normal
3	$2\sigma^{-1}1\pi^{-1}2\pi^1 {}^2\Delta, {}^2\Sigma^-$	306.31	conjugate
4	$2\sigma^{-1}4\sigma^{-1}2\pi^1 {}^2\Pi$	308.97	conjugate
5	$2\sigma^{-1}1\pi^{-1}2\pi^1(S' = 0)^2\Sigma^-$	311.29	normal
6	unknown	313.30	conjugate
7	$2\sigma^{-1}5\sigma^{-1}6\sigma^1(S' = 1)^2\Sigma^+$	313.97	normal
8	$2\sigma^{-1}5\sigma^{-1}6\sigma^1(S' = 0)^2\Sigma^+$	315.37	normal
9	$2\sigma^{-1}5\sigma^{-1}7\sigma^1(S' = 1)^2\Sigma^+$	316.25	normal
10	unknown	317.14	normal

TABLE I: CO C 1s ionized ground and excited electronic states (from [24]). The assignment of the type of shake up state is taken from the β parameter of the photoelectron from [24]. States assigned as "conjugate" are those for which a β close to zero has been observed.

lines in Table 1 together with the assignment of their symmetry and their suggested type of shake up (normal or conjugate).

The ion electron coincidence allows us to split our data set into two subsets. The first one consists of events where the orientation of the molecule is parallel, the second one includes only events where the orientation is perpendicular to the polarization. These are shown in Fig. 1 (b),(c). Clearly, line number 6 is almost missing for parallel orientation. This shows that the mechanism responsible for the excitation of the conjugate configuration is excitation by photon absorption followed by shake up and not PEVE. This is different to the case of CO₂, where satellites have been reported in [8] which - despite of being of conjugate type - are populated mainly when the molecule and the polarization vector of the light are in parallel.

The two color panels (d),(e) in Fig. 1 show the angular distribution in the molecular frame for parallel and perpendicular orientation. They strongly vary as function of electron energy. As the angular distributions are created by multiple scattering and interference, they depend on the electron wavelength. To separate the effects caused by different electron wavelengths from effects of the satellite excitation we have performed our experiment at different photon energies, chosen such that the electron energy for the line under investigation is always about 10 eV. We picked the main line and the prominent lines 4, 5 and 7 to compare their angular distributions in the molecular frame which are shown in Figure 2. An electron energy of 10 eV is in the range of the Σ shape resonance for the main line [41, 42]. The angular distribution in Fig. 2(a) for parallel orientation shows the well known "guitar-like" shape with the main lobe in the direction of the Oxygen atom. Additional lobes at around 60 deg result from a strong contribu-

tion of an f -wave which is characteristic for this shape resonance. The two normal satellites 5 and 7 for which the final state is of the same Σ symmetry as the main line show a qualitatively similar pattern. The angular distributions show that the satellites exhibit a very similar shape resonance as the main line, confirming similar claims of a shape resonance in satellites made in [25, 27, 28, 32]. It is worth noting that the molecular frame angular distribution of the main line and the two satellites of the same symmetry are not exactly equal. The multiple scattering is very sensitive to the details of the potential and to vibrational excitation [43–46]. Both are slightly different for the satellites, giving rise to the variations in the angular distribution. Most interesting is the angular distribution of peak number 4 (Fig. 2(d)) which is a conjugate shake up to a state of Π symmetry. In this case, as well, the body fixed frame angular distribution is similar to the main line, but in that case the angular distribution is plotted for perpendicular orientation of the molecule. The shape of the angular distribution found here strongly resembles the characteristics of a Σ shape resonance. The Σ , however, refers to the symmetry of the continuum orbital. To reach this orbital by conjugate shake up the polarization has to be perpendicular to the molecular axis. This shows that also conjugate shake up satellites experience a Σ shape resonance at similar electron energies of the main line - for the Π orientation. This is in line with the generalization of the atomic shake up model to states with molecular symmetry mentioned above. The shake up matrix element is purely a (monopole) overlap of the bound 4σ orbital to the $\epsilon\sigma$ continuum state which forms the shape resonance. This can even be rationalized approximately from atomic states which are by multiple scattering converted to molecular continuum states with higher angular momentum, since the bound 4σ orbital roughly resembles an atomic $2p_z$ orbital. As the electron from this orbital is shaken off it creates a p_z wave in the continuum very much like for the main line where this wave is created by photoejection if the molecular axis is parallel to the polarization. This p_z wave is subsequently multiply scattered adding the higher angular momenta visible in *guitar-*

like shapes in figure 2.

IV. CONCLUSIONS

Our data give a very clear general trend: the molecular frame angular distribution of the satellites in K-shell ionization of CO are very similar to the angular distribution of the main line at the same electron energy and at the same symmetry. I.e. a σ like pattern as for the main line is found if molecule and polarization are parallel. The same pattern evolves for satellites where the remaining $\text{CO}^{+*}(\text{C}1s^{-1})$ has the same σ symmetry as the $\text{CO}^+(\text{C}1s^{-1})$, while for satellites where the $\text{CO}^{+*}(\text{C}1s^{-1})$ has Π symmetry a strikingly similar pattern arises if the polarization is perpendicular to the molecular axis. As shape resonances manifest themselves nicely in the body fixed frame angular distributions, the satellites show equivalent shape resonances as the main line. These observations can be reconciled with a two step model of photo absorption followed by shake up and a multiple scattering of the continuum electron in the molecular potential.

Acknowledgments

This work was supported by DFG, the Division of Chemical Sciences, Geosciences and Biosciences Division, Office of Basic Energy Sciences, Office of Science, U. S. Department of Energy and the Director, Office of Science, Office of Basic Energy Sciences and Division of Materials Sciences under U.S. Department of Energy Contract No. DE-AC03-76SF00098. We are grateful for excellent support during the beamtime by Elke Arenholz and Tony Young. We are deeply indebted to an unknown referee of our paper, who has pointed out a serious mistake in our interpretation and has suggested the molecular version of the shake off as we describe it now in the final version of this paper.

-
- [1] T.A. Carlson and M.O. Krause. *Phys. Rev.*, **140**:1057, 1965.
 - [2] Teijo Åberg. *Phys. Rev.*, **A156**(1):35–41, 1967.
 - [3] Ken-ichi Hino, T. Ishihara, F. Shimizu, N. Toshima, and J.H. McGuire. *Phys. Rev.*, **A48**:1271, 1993.
 - [4] J.H. McGuire, N. Berrah, R.J. Bartlett, J.A.R. Samson, J.A. Tanis, C.L. Cocke, and A.S. Schlachter. *J. Phys.*, **B28**:913, 1995.
 - [5] A. Dalgarno and H.R. Sadeghpour. *Phys. Rev.*, **A46**:R3591, 1992.
 - [6] T. Schneider, P.L. Chician, and J.M. Rost. *Phys. Rev. Lett.*, **89**:073002, 2002.
 - [7] T. Schneider and J.M. Rost. *Phys. Rev.*, **A67**:062704, 2003.
 - [8] X.-J. Liu, H. Fukuzawa, T. Teranishi, A. De Faniis, M. Takahashi, H. Yoshida, A. Cassimi, A. Czasch, L. Schmidt, R. Dörner, I. Koyano, N. Saito, and K. Ueda. *Phys. Rev. Lett.*, **101**(2):023001, 2008.
 - [9] A. A. Pavlychev. *J. Phys.*, **32**(9):2077–2088, 1999.
 - [10] A. De Faniis, N. Saito, A. A. Pavlychev, D. Yu. Ladonin, M. Machida, K. Kubozuka, I. Koyano, K. Okada, K. Ikejiri, A. Cassimi, A. Czasch, R. Dörner, H. Chiba, Y. Sato, and K. Ueda. *Phys. Rev. Lett.*, **89**(2):023006, 2002.

- [11] A. Becker and F.H.M. Faisal. *J. Phys.*, **B38**:R1, 2005.
- [12] A. Knapp, A. Kheifets, I. Bray, Th. Weber, A.L. Landers, S. Schössler, T. Jahnke, J. Nickles, S. Kammer, O. Jagutzki, L.Ph. Schmidt, T. Osipov, J. Rösch, M.H. Prior, H. Schmidt-Böcking, C.L. Cocke, and R. Dörner. *Phys. Rev. Lett.*, **89**:033004 1–4, 2002.
- [13] I.G. Kaplan and A.P. Markin. *Sov. Phys. Dokl.*, **14**:36–39, 1969.
- [14] J.L. Dehmer and D. Dill. *Phys. Rev. Lett.*, **35**:213, 1975.
- [15] H. C. Choi, R. M. Rao, A. G. Mihill, S. Kakar, E. D. Poliakoff, K. Wang, and V. McKoy. *Phys. Rev. Lett.*, **72**:44, 1994.
- [16] A.L. Landers, Th. Weber, I. Ali, A. Cassimi, M. Hattass, O. Jagutzki, A. Nauert, T. Osipov, A. Staudte, M. H. Prior, H. Schmidt-Böcking, C. L. Cocke, and R. Dörner. *Phys. Rev. Lett.*, **87**:013002, 2001.
- [17] E. Shigemasa, J. Adachi, M. Oura, and A. Yagishita. *Phys. Rev. Lett.*, **74**:359, 1995.
- [18] M. S. Schöffler, J. Titze, N. Petridis, T. Jahnke, K. Cole, L. Ph. H. Schmidt, A. Czasch, D. Akoury, O. Jagutzki, J. B. Williams, N. A. Cherepkov, S. K. Semenov, C. W. McCurdy, T. N. Rescigno, C. L. Cocke, T. Osipov, S. Lee, M. H. Prior, A. Belkacem, A. L. Landers, H. Schmidt-Böcking, Th. Weber, and R. Dörner. *Science*, **320**:920, 2008.
- [19] D. Akoury, K. Kreidi, T. Jahnke, Th. Weber, A. Staudte, M. Schöffler, N. Neumann, J. Titze, L. Ph. H. Schmidt, A. Czasch, O. Jagutzki, R. A. Costa Fraga, R. E. Grisenti, R. Diez Muino, N. A. Cherepkov, S. K. Semenov, P. Ranitovic, C. L. Cocke, T. Osipov, H. Adaniya, J. C. Thompson, M. H. Prior, A. Belkacem, A. Landers, H. Schmidt-Böcking, and R. Dörner. *Science*, **319**:949, 2007.
- [20] J. Fernandez, O. Fojon, A. Palacios, and F. Martn. *Phys. Rev. Lett.*, **98**:043005–1 – 043005–4, 2007.
- [21] K. Kreidi, D. Akoury, T. Jahnke, Th. Weber, A. Staudte, M. Schöffler, N. Neumann, J. Titze, L. Ph. H. Schmidt, A. Czasch, O. Jagutzki, R.A. Costa Fraga, R.E. Grisenti, P. Ranitovic M. Smolarski, C.L. Cocke, T. Osipov, H. Adaniya, J.C. Thompson, M.H. Prior, A. Belkacem, A. Landers, H. Schmidt-Böcking, and R. Dörner. *Phys. Rev. Lett.*, **100**:133005, 2008.
- [22] M.S. Schöffler, K. Kreidi, D. Akoury, T. Jahnke, A. Staudte, N. Neumann, J. Titze, L.Ph.H. Schmidt, A. Czasch, O. Jagutzki, R.A. CostaFraga, R.E. Grisenti, M. Smolarski, P. Ranitovic, C.L. Cocke, T. Osipov, H. Adaniya, S. Lee, J.C. Thompson, M.H. Prior, A. Belkacem, Th. Weber, A. Landers, H. Schmidt-Böcking, and R. Dörner. *Phys. Rev.*, **A78**(013414), 2008.
- [23] K. Ueda, M. Hoshino, T. Tanaka, M. Kitajima, H. Tanaka, A. De Fanis, Y. Tamenori, M. Ehara, F. Oyagi, K. Kuramoto, and H. Nakatsuji. *Phys. Rev. Lett.*, **94**:243004, 2005.
- [24] O Hemmers, S B Whitfield, N Berrah, B Langer, R Wehlitz, and U Becker. *J. Phys.*, **B28**(22):L693–L700, 1995.
- [25] L. Ungier and T. D. Thomas. *Phys. Rev. Lett.*, **53**(5):435–438, 1984.
- [26] K. J. Randall, A. L. D. Kilcoyne, H. M. Köppe, J. Feldhaus, A. M. Bradshaw, J.-E. Rubensson, W. Eberhardt, Z. Xu, P. D. Johnson, and Y. Ma. *Phys. Rev. Lett.*, **71**(8):1156–1159, 1993.
- [27] A. Reimer, J. Schirmer, J. Feldhaus, A. M. Bradshaw, U. Becker, H. G. Kerkhoff, B. Langer, D. Szostak, R. Wehlitz, and W. Braun. *Phys. Rev. Lett.*, **57**(14):1707–1710, 1986.
- [28] T. Reich, P. A. Heimann, B. L. Petersen, E. Hudson, Z. Hussain, and D. A. Shirley. *Phys. Rev.*, **A49**(6):4570–4577, 1994.
- [29] M. Ehara, K. Kuramoto, H. Nakatsuji, M. Hoshino, T. Tanaka, M. Kitajima, H. Tanaka, A. De Fanis, Y. Tamenori, and K. Ueda. *J. Chem. Phys.*, **125**:114304,(2006)
- [30] G. Angonoa, O. Walter, and J. Schirmer. *J. Chem. Phys.*, **87**(12):6789–6801, 1987.
- [31] G. Bandarage and R.R. Lucchese. *Phys. Rev.*, **A47**(3):1989–2003, 1993.
- [32] J. Schirmer, M. Braunstein, and V. McKoy. *Phys. Rev.*, **144**:5762, 1991.
- [33] J. Schirmer, G. Angonoa, S. Svensson, D. Nordsfors, and U. Gelius. *J. Phys.*, **B60**31:377, 1987.
- [34] R. Dörner, V. Mergel, O. Jagutzki, L. Spielberger, J. Ullrich, R. Moshhammer, and H. Schmidt-Böcking. *Physics Reports*, **330**:96–192, 2000.
- [35] J. Ullrich, , R. Moshhammer, A. Dorn, R. Dörner, L. Ph. Schmidt, and H. Schmidt-Böcking. *Rep. Prog. Phys.*, **66**:1463–1545, 2003.
- [36] T. Jahnke, Th. Weber, T. Osipov, A.L. Landers, O. Jagutzki, L.Ph.H. Schmidt, C.L. Cocke, M.H. Prior, H.Schmidt-Böcking, and R.Dörner. *Journal of Electron Spectroscopy and Related Phenomena*, **141**:229, 2004.
- [37] O. Jagutzki, V.Mergel, K. Ullmann-Pfleger, L. Spielberger, U. Spillmann, R. Dörner, and H. Schmidt-Böcking. *Nucl. Instr. Meth.*, **A477**:244–249, 2002.
- [38] see Roentdek.com for details of the detectors.
- [39] T. Weber, O. Jagutzki, M. Hattass, A. Staudte, A. Nauert, L. Schmidt, M.H. Prior, A.L. Landers, A. Bräuning-Demian, H. Bräuning, C.L. Cocke, T. Osipov, I. Ali, R. Diez Muino, D. Rolles, F.J. Garcia de Abajo, C.S. Fadley, M.A. Van Hove, A. Cassimi, H. Schmidt-Böcking, and R. Dörner. *J. Phys.*, **B34**:3669, 2001.
- [40] Th. Weber, M. Weckenbrock, M. Balser, L. Schmidt, O. Jagutzki, W. Arnold, O. Hohn, E. Arenholz, T. Young, T. Osipov, L. Foucar, A. De Fanis, R. Diez Muino, H. Schmidt-Böcking, C. L. Cocke, M. H. Prior, and R. Dörner. *Phys. Rev. Lett.*, **90**:153003, 2003.
- [41] E. Shigemasa, J. Adachi, , K. Soejima, N. Watanabe, A. Yagishita, and N.A. Cherepkov. *Phys. Rev. Lett.*, **80**:1622, 1998.
- [42] T. Jahnke, Th. Weber, A. L. Landers, A. Knapp, S. Schössler, J. Nickles, S. Kammer, O. Jagutzki, L. Schmidt, A. Czasch, T. Osipov, E. Arenholz, A. T. Young, R. Diez Muino, D. Rolles, F. J. Garcia de Abajo, C. S. Fadley, M. A. Van Hove, S.K. Semenov, N.A. Cherepkov, J. Rösch, M. H. Prior, H. Schmidt-Böcking, C. L. Cocke, and R. Dörner. *Phys. Rev. Lett.*, **88**:073002, 2002.
- [43] J. Adachi, K. Hosaka, S. Furuya, K. Soejima, M. Takahashi, A. Yagishita, S.K. Semenov, and N.A. Cherepkov. *Phys. Rev. Lett.*, **91**:163001, 2003.
- [44] T. Jahnke, L. Foucar, J. Titze, R. Wallauer, T. Osipov, E.P. Benis, A. Alnaser, O. Jagutzki, W. Arnold, S.K. Semenov, N.A. Cherepkov, L.Ph.H. Schmidt, A. Czasch, A. Staudte, M. Schöffler, C.L. Cocke, M.H. Prior, H. Schmidt-Böcking, and R. Dörner. *Phys. Rev. Lett.*, **93**:083002, 2004.

- [45] S. K. Semenov, N. A. Cherepkov, T. Jahnke, and R. Dörner. *J. Phys.*, B37:1331, 2004.
- [46] S. K. Semenov, N. A. Cherepkov, M. Matsumoto, K. Fujiware, K. Ueda, E. Kukk, F. Tahara, T. Sunami, H. Yoshida, T. Tanaka, K. Nakagawa, M. Kitajima, H. Tanaka, and A. De Fanis. *J. Phys.*, B39:375, 2006.
- [47] E. J. Moler, S. A. Kellar, Z. Hussain, Y. F. Chen, D. A. Shirley, W. R. A. Huff, and Z. Q. Huang. *Phys. Rev.*, B56(24):16016–16020, 1997.

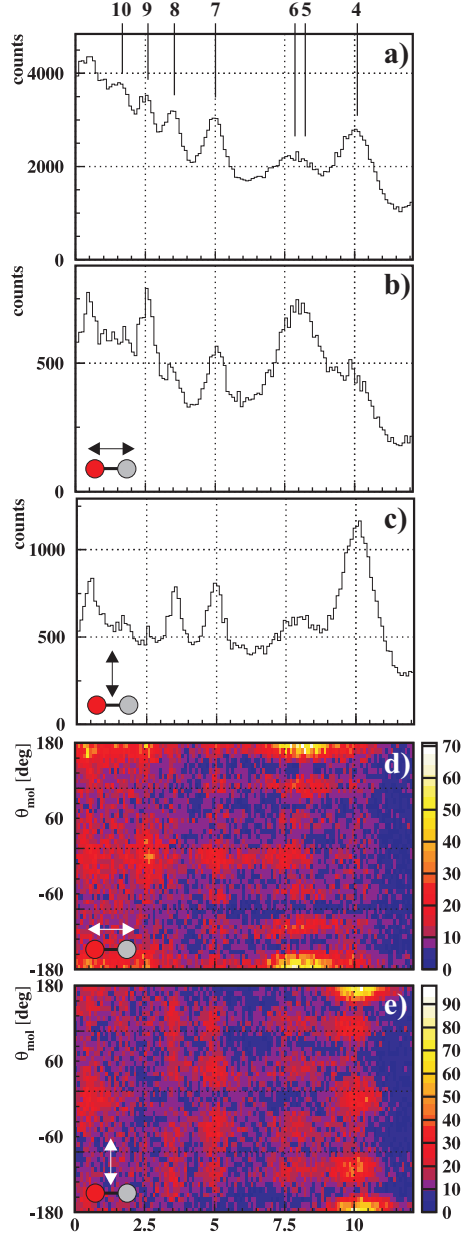


FIG. 1: C K-shell ionization of CO at a photon energy of 318.97 eV. (a) electron energy distribution integrated over all electron and all ion emission angles. (b) as (a) but for molecules being oriented parallel to the polarization. (c) same but for molecules being aligned perpendicularly to the polarization. (d) electron energy versus angle of the electron in the body fixed frame of the molecule, zero degree is the direction of the Oxygen. Molecule and polarization vector of the light are in parallel. (e) same as (d) but for molecules that are oriented perpendicularly to the polarization.

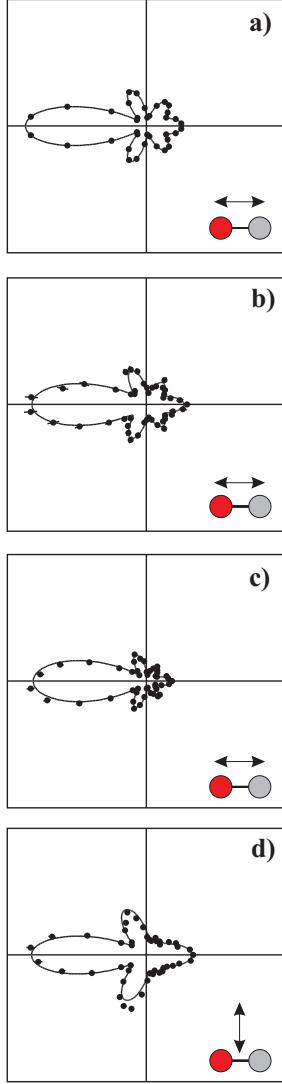


FIG. 2: Angular distribution of the main line (a) the normal satellite lines 5 (b) and 7 (c) and the conjugate line 4 (d) (see Table 1 for numbering of the lines). For (a), (b) and (c) the polarization is parallel to the molecular axis, for (d) it is perpendicular. The lines show fits of Legendre polynomials to guide the eye. The photon energy is 306.0 eV, 323.97 eV, 321.29 eV, 318.97 eV in panels (a), (b), (c), (d) chosen such that the electron energy is about 10 eV in all four cases. The icons show the orientation of the molecule and the polarization vector of the light; the Oxygen atom is on the left.